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Quarterly Report

January 1, 1985 - March 31, 1985

for the contract

USE OF LOW ENERGY HYDROGEN ION IMPLANTS IN HIGH  
EFFICIENCY CRYSTALLINE SILICON SOLAR CELLS

Contract No. 957126

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## Summary

The first quarter of this study has concentrated on Tasks #1 and #2 of our program. Specifically, the effects of hydrogen implants, made through the front surface of a cell structure, on emitter properties were examined as were the effects of  $H^+$  implants on Si regrowth and diffusion. Although hydrogen implants can passivate dangling bonds at the emitter surface and in the emitter, they can also create structural damage, can potentially deactivate dopants, and can introduce recombination centers in the emitter. We report here that, for the implant parameters used in this study, the hydrogen beam exposure was found to passivate the emitter surface essentially as effectively as an oxide layer. That is, the emitter bucking (dark) current is found to be essentially the same if the emitter surface is passivated with an oxide or with a hydrogen implant. However, the emitter contribution to the photocurrent suffers due to hydrogen implants. This is shown to be blue response loss. We tentatively model this situation as follows: The strongly absorbing, amorphous layer at the surface created by the  $H^+$  implant absorbs in the blue and has a very poor lifetime; however, its presence passivates the surface of the emitter existing below this implanted layer.

In the work done on examining the effect of hydrogen on silicon regrowth, it was found that the presence of hydrogen did not affect the regrowth of  $As^+$  implanted layers. In the studies done to determine if hydrogen implants can alter diffusion, it was found the hydrogen, implanted after  $As^+$ , does not alter As diffusion. However, hydrogen, implanted after  $BF_2^+$ , does alter B

diffusion. This clearly has important consequences for shallow junction formation in solar cell structures and is under further investigation.

## Quarterly Report for Contract No. 957126

### I. Introduction

This program is a study of the use of low energy hydrogen ion implantation for high efficiency crystalline silicon solar cells. The program is under the direction of Dr. S. J. Fonash, Professor of Engineering Sciences. Ranbir Singh, a doctoral student in Solid State Science, is the Research Assistant.

The first Quarterly Report focuses on two tasks of this JPL program:

(1) an examination of the effects of low energy hydrogen implants on surface recombination speed and (2) an examination of the effects of hydrogen on silicon regrowth and diffusion in silicon. The first of these two tasks is discussed in Section II; the second is the subject of Section III.

### II. Effects of $H^+$ implants on surface properties

The first part of the project focussed on the measurement of surface properties of hydrogen implanted silicon. Low energy hydrogen ions when bombarded on the silicon surface will create structural damage at the surface, deactivate dopants and introduce recombination centers. At the same time the electrically active centers such as dangling bonds will be passivated by these hydrogen ions. Thus hydrogen is expected to alter properties such as the surface recombination velocity, dopant profiles on the emitter, etc. In this report the surface recombination velocity of a hydrogen implanted emitter was measured.

#### A. Experimental data:

For this study a solar cell (4412-5C) made by Spire Corporation was used. Doping profile of a similarly processed solar cell is shown in Fig. 1.<sup>[1]</sup>

Boron concentration in the base was  $10^{17} \text{ cm}^{-3}$ . Front surface of this device was passivated with a  $256 \text{ \AA}$  thick oxide layer. The spectral response of this device was measured and the quantum efficiency (QE) is shown in Figure 2. Dark I-V characteristics of this device were measured. The recombination current was subtracted from the measured current and the series resistance effects were taken into account when determining the diode voltage drop. Figure 3 shows the  $\log(I - I_{\text{rec}})$  vs  $(V - IR_s)$  characteristics of this device. Also shown on the figure are the characteristics of this cell after stripping the passivating oxide with a 2% HF solution. Finally, the device was implanted with 0.4 keV hydrogen ions at normal incidence to a dose of  $\sim 10^{18} \text{ cm}^{-2}$ . The spectral response was again measured and is plotted in Fig. 4. Figure 5 shows the  $\log(I - I_{\text{rec}})$  vs  $(V - IR_s)$  plot after the hydrogen implantation.

## B. Data Analysis

### 1. Decomposition of emitter and base currents

Extrapolating the  $\log(I - I_{\text{rec}})$  vs  $V_d$ , where  $V_d = V - IR_s$ , to  $V_d = 0$ , the saturation current  $J_0$  of diode can be determined from the y intercept of this plot.

$$J_0 = J_{\text{ob}} + J_{\text{oe}}$$

where  $J_0$  = total saturation current

$J_{\text{ob}}$  = component of the saturation current due to base transport

$J_{\text{oe}}$  = component of the saturation current due to emitter transport

$$J_{\text{ob}} = \frac{q n_i^2 D_n}{N_A \cdot L_n} \cdot \frac{\frac{S n_i L_n}{D_n} + \tanh \frac{W_b}{L_n}}{1 + \frac{S n_i L_n}{D_n} \tanh \frac{W_b}{L_n}}$$

1

Since in our device  $W_b$  is greater than  $3 L_n$ , the expression reduces to

$$J_{ob} = \frac{q n_i^2 D_n}{N_A \cdot L_n}$$

2

$L_n$  is measured from the red response of the solar cell and was determined to be  $\approx 98 \mu m$ . This did not change with processing of the device. To be consistent, in our modelling involving heavy doping effect where minority carrier mobility data is not available, the majority and minority carrier mobilities and diffusivities were assumed to be the same. The diffusivities were calculated from expression given by Engl.<sup>[2]</sup> With the above parameters  $J_{ob}$  was calculated and subtracted from  $J_o$  to determine  $J_{oe}$ . The results are shown in Table I.

## 2. Analysis of the emitter component of saturation current

For a shallow emitter such as that of cell 4412-5C, the transit time of injected carriers, across the emitter, is extremely small compared to their life-time. This allows one to use the transparent emitter approximation where carrier loss due to recombination is neglected, and the injected current density is assumed to be constant. It can be easily shown that in this case

$$J_{oe} = \frac{q n_i^2}{\int_0^{W_E} \frac{N_D(x) n_i^2}{n_{ieff}^2(x)} \cdot \frac{1}{D_p(x)} dx + \frac{N_D(0)}{S_p} \cdot \frac{n_i^2}{n_{ieff}^2(0)}}$$

3

where  $N_D(n)$  is the emitter doping profile,  $D_p$  is the hole diffusivity, and  $S_p$  is the surface recombination velocity and  $n_{ieff}(x)$  is the effective "intrinsic" carrier density, which takes heavy doping effects into account. Large discrepancies exist between theoretically calculated and experimentally measured values of  $n_{ieff}$ . For the analysis in this report we chose the emper-

ical formula provided by Roulston.<sup>[3]</sup> The carrier degeneracy in the emitter was accounted for by using the analytical formulae provided by Blakemore.<sup>[4]</sup> A computer program that evaluates the integral in the denominator of Eq. 3 was written and  $S_p$  values were extracted. The results are shown in Table II. While doing these calculations we found that the contribution of the integral to the denominator of Eq. 3 was negligible, indicating that it is possible to reduce the emitter width, without adversely affecting the emitter characteristics. This should enhance the blue response of the cell.

#### Spectral response analysis:

Comparing the quantum efficiency (QE) of the devices with the passivating oxide to the QE of the hydrogen implanted solar cell we find that the blue response has degraded considerably. This may at first seem anomalous since the  $S_p$  does not show a significant deviation for these two cases. However, recognizing the fact that hydrogen creates a heavily disordered layer  $\sim 200$  Å thick at the surface we speculate that the layer provides very efficient recombination sites for photogenerated carriers and hence results in a poorer response in the blue spectral region. Further modelling to quantify the loss of the blue response is now underway.

#### III. Regrowth and diffusion studies

High dose implants encountered during the emitter formation of solar cells usually render this region amorphous. The crystallineity of the damaged layer is recovered through a relatively low temperature (550-600°C) anneal and the dopant is activated using a high temperature ( $\sim 900^\circ\text{C}$ ) anneal. Significant diffusion can occur at these high temperatures, especially for the fast diffusing species such as boron. The effect of hydrogen in modifying the diffusion characteristics of the dopant was investigated in this report. In addition,



there is considerable interest in the regrowth kinetics of amorphized layers. It is been suggested that the regrowth velocity of these amorphized layers is dependent on the change of the defects at the regrowth interface. Since we have already showed that hydrogen implants can remove these charged states by tying up the dangling bonds, it was speculated that the regrowth velocity of the amorphized layer may be altered, if the regrowth anneal was performed after a hydrogen implant. This hypothesis was also tested.

#### A. Regrowth of amorphized layers

High dose ( $5 \times 10^{15} \text{ cm}^{-2}$ ) As implants at 180 keV were used to create the damaged layers. Half of As implanted samples were further implanted with 0.4 keV hydrogen (dose  $10^{18} \text{ cm}^{-2}$ ) and then annealed at 500°C for various times. The thickness of the amorphized layer was measured using backscattering spectrometry in the channelling mode. In all these samples the thickness of the amorphous layer created due to the arsenic implants was much greater than that could be created by the subsequent hydrogen implant. Regrowth rates of amorphized layer containing hydrogen were not found to be significantly different from those of the control set (no hydrogen implant before anneal). One can then conclude that hydrogen does not affect the regrowth of amorphized layers at the temperatures normally used for this purpose.

#### B. Diffusion Studies

Diffusion studies of arsenic and boron during the regrowth and activation anneal are now discussed. As ( $75 \text{ keV}, 5 \times 10^{15} \text{ cm}^{-2}$ ) or  $\text{BF}_2^+$  ( $50 \text{ keV}, 5 \times 10^{15} \text{ cm}^{-2}$ ) was implanted into silicon to create the amorphous layers.  $\text{BF}_2^+$  was used in this study since boron implants alone do not yield amorphous layers at the surface. Use of  $\text{BF}_2^+$  also avoids the deep tails usually seen in boron implanted silicon and hence, shallower junctions are possible.

Following the dopant implant, low energy hydrogen ions at 0.4 keV, were implanted into some of these samples. These samples were then annealed at 500°C or 600°C or were subjected to a three step anneal consisting of a 550°C two hour anneal + 900°C 15 minute anneal + 550°C two hour anneal. The dopant profiles were obtained using SIMS.

In the case of arsenic, as expected, there was no substantial diffusion of the dopant even after the 900°C anneal. Samples that had no hydrogen in them did not reveal any different dopant profiles from those that were implanted with hydrogen. Boron, however, showed that hydrogen implants before the anneal could alter its diffusion characteristics.

Figure 6 shows the boron profile obtained after various annealing steps. Diffusion of boron at 500°C and 600°C is not observable and shows no dependence on the hydrogen content in the sample. Profile 6b is obtained from the sample that did not have any hydrogen in it and saw a three step anneal. Some dopant redistribution is evident. The most significant result of this investigation is seen in 6c, which shows that the implantation of hydrogen can alter the diffusion of boron even at temperatures as high as 900°C. Computer modelling of the dopant redistribution taking concentration dependent dopant diffusivity into account shows that the enhanced diffusion cannot be explained by simple diffusion. Refinements to this model are currently being made.

#### IV. Conclusions

1. Although  $H^+$  implants can yield layers with surface recombination velocity that is comparable to that with an oxide, the degradation of the blue response makes the use of this process unattractive. Hence one must remove this layer by chemically etching the surface to remove a layer  $\sim 200 \text{ \AA}$  thick.

Since our analysis shows that the emitter current is controlled entirely by the surface recombination velocity, decrease in the emitter width due to etching should not adversely affect the leakage currents.

2. Taking this result in conjunction with our earlier results on solar cells made on Westinghouse web silicon we can conclude that hydrogen implants will be good for improvement of the base properties of cells made on non-crystalline materials. In addition, if hydrogen is implanted in ion-implanted silicon solar cell before the activation anneal leakage currents should improve in a manner analogous to results reported in [5].

3. SIMS profiles of silicon surfaces after  $H^+$  implants showed an increase in the oxygen content in these implanted layers. More work is needed to determine if this oxygen enters during or after (on exposure to air) the  $H^+$  implant.

4. Hydrogen can significantly alter the diffusion of boron in silicon. This result seems a little surprising since it is generally accepted that hydrogen out diffuses from silicon at relatively low temperatures ( $\sim 400^\circ C$ ), and so should not affect diffusion of boron for the three step anneal used in this study. Further investigations to unravel this anomalous diffusion are in progress.

5. Hydrogen, for the re-growth temperatures explored, did not affect regrowth after As implants. We were not able to study regrowth of Si implanted silicon due to difficulty getting samples. This work has been postponed.

#### Acknowledgements

The authors would like to thank M. B. Spitzer of Spire Corporation for valuable assistance in certain aspects of this investigation.

## V. Projected Activities

The aspects of Tasks #1 and #2 that need additional study will be addressed in the next three months. Specifically, as noted, we discovered using SIMS that  $H^+$  implanted layers contain oxygen. We will endeavor to determine when this oxygen enters the layer and its roll. As noted, we were not able to obtain  $Si^+$  implanted silicon for regrowth studies; consequently, we only studied regrowth for  $As^+$  implanted silicon. However,  $Si^+$  implanted samples will be obtained and studied. Since no effect of regrowth for  $As$  implanted silicon was seen, we do not expect  $H^+$  implants to affect the regrowth of  $Si^+$  implanted silicon.

In the next three months work will continue on Tasks #3 and #4. Work will begin on Tasks #5 and #6 at about the sixth month when our base of knowledge will insure effective implementation of these tasks.

TABLE I

| Processing                               | $J_o$ (pA/cm <sup>2</sup> ) | $J_{oe}$ (pA/cm <sup>2</sup> ) |
|--|-----------------------------|--------------------------------|
| 4412-5C as is                            | 3.78                        | 1.71                           |
| 4412-5C no oxide                         | 7.13                        | 5.06                           |
| 4412-5C no oxide<br>after H <sup>+</sup> | 3.90                        | 1.83                           |

$J_{ob} = 2.07 \times 10^{-12} \text{ A/cm}^2$

TABLE II

| Model    | $S_p$ with<br>oxide | $S_p$ no<br>oxide  | $S_p$ no oxide<br>with H <sup>+</sup> |
|----------|---------------------|--------------------|---------------------------------------|
| Roulston | $1.53 \times 10^4$  | $5.66 \times 10^4$ | $1.65 \times 10^4$                    |

$$J_{oe} \text{ (with oxide)} = 3.786 \times 10^{-12} \text{ A/cm}^2.$$

$$J_{oe} \text{ (without oxide)} = 7.13 \times 10^{-12} \text{ A/cm}^2.$$

$$J_{oe} \text{ (no oxide + 0.4 keV H}^+) = 3.90 \times 10^{-12} \text{ A/cm}^2.$$

## References

1. M. B. Spitzer, C. J. Kearney, S. P. Tobin, F. A. Lindholm, A. Neugroschel, 17th IEEE Photovoltaic Specialists Conference, May 1-4, 1984.
2. W. L. Engl, H. K. Dirks, and Bernd Meinerzhagen, Proc. of IEEE, Vol. 71, 1983.
3. D. R. Roulston, N. D. Arora, S. G. Chamberlain, IEEE Trans. on Elec. Devices, T-ED 29, 284, 1982.
4. J. S. Blakemore, Solid State Elec., Vol. 25, 1067, 1982.
5. R. Singh, S. J. Fonash, A. Rohatgi, P. Rai-Choudhury, and J. Gigante, J. Appl. Phys., Vol. 55, 807, 1984.

## List of Figures

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4. Log  $(I - I_{rec})$  vs  $(V - IR_s)$  for the same device after an  $H^+$  implantation.
5. Spectral response of the solar cell after the hydrogen implant.
6. Boron profiles in Si implanted with  $BF_2^+$  and then processed as below.
  - a. As implanted device. The profile after a  $600^\circ C$  one hour anneal is also similar.
  - b. Sample annealed using a three step anneal. This sample was not  $H^+$  implanted.
  - c. Sample was implanted with hydrogen after the dopant implant. The profile shown was obtained after the three step anneal.

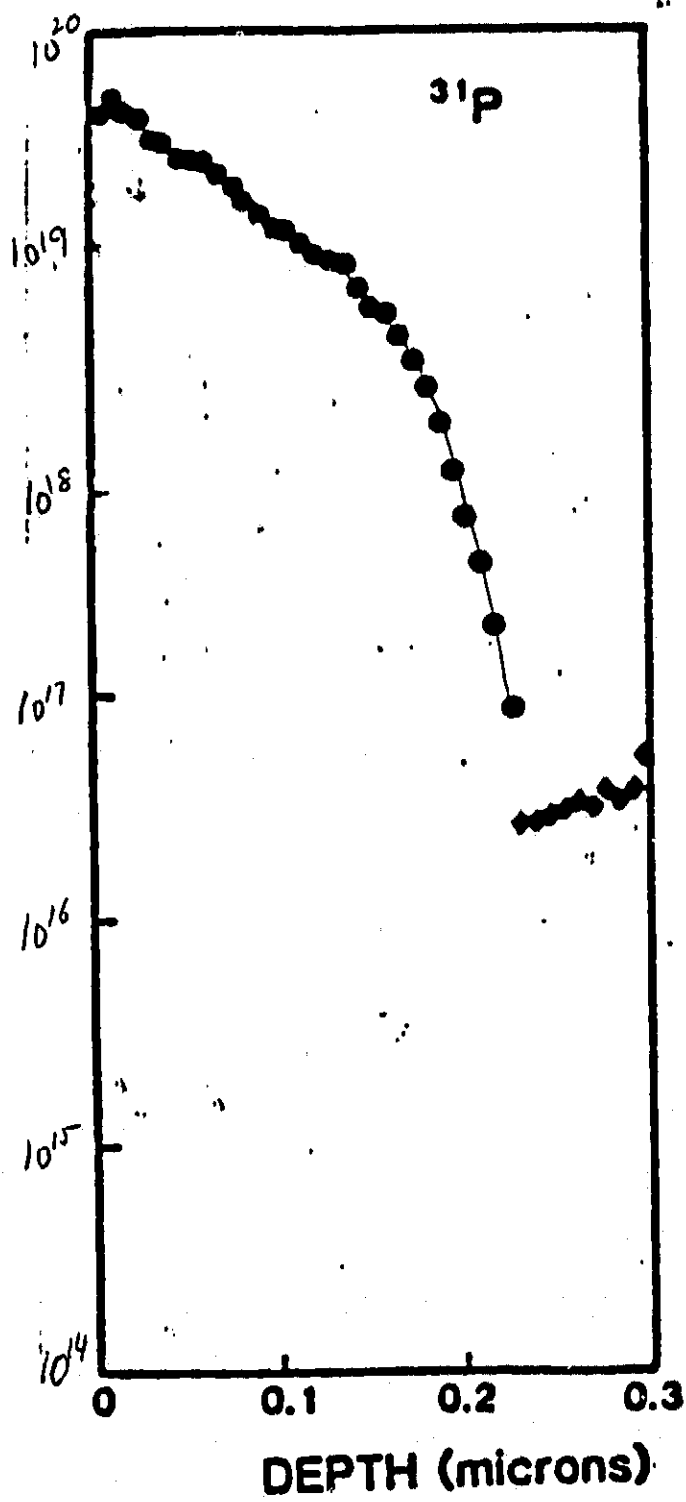


Fig A.



ORIGINAL PAGE IS  
OF POOR QUALITY

EXTERNAL QUANTUM EFFICIENCY  
Cell: 4412-5C 09-AUG-84 16:22:07  
area: 4 cm<sup>2</sup> standard: 2706-26

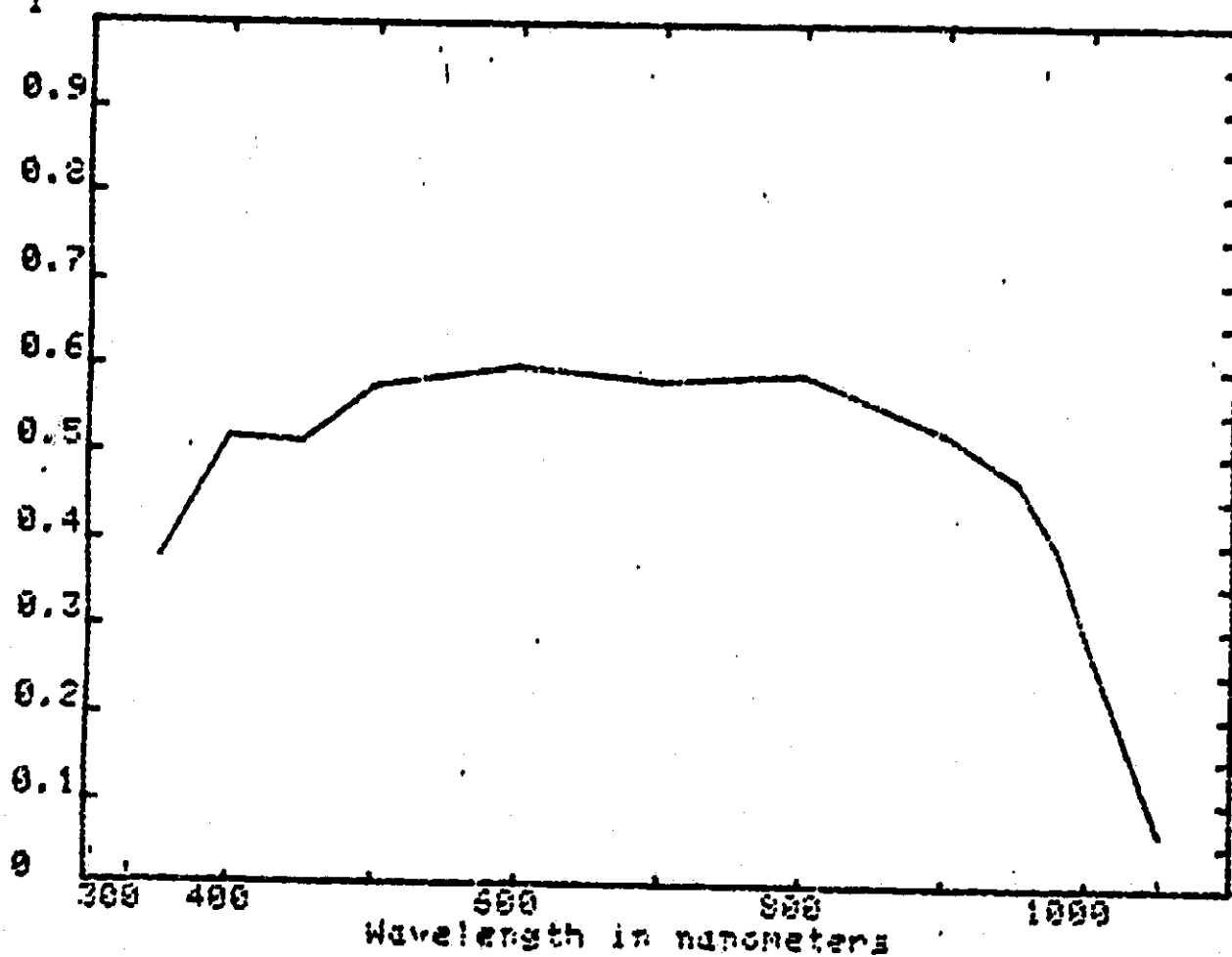
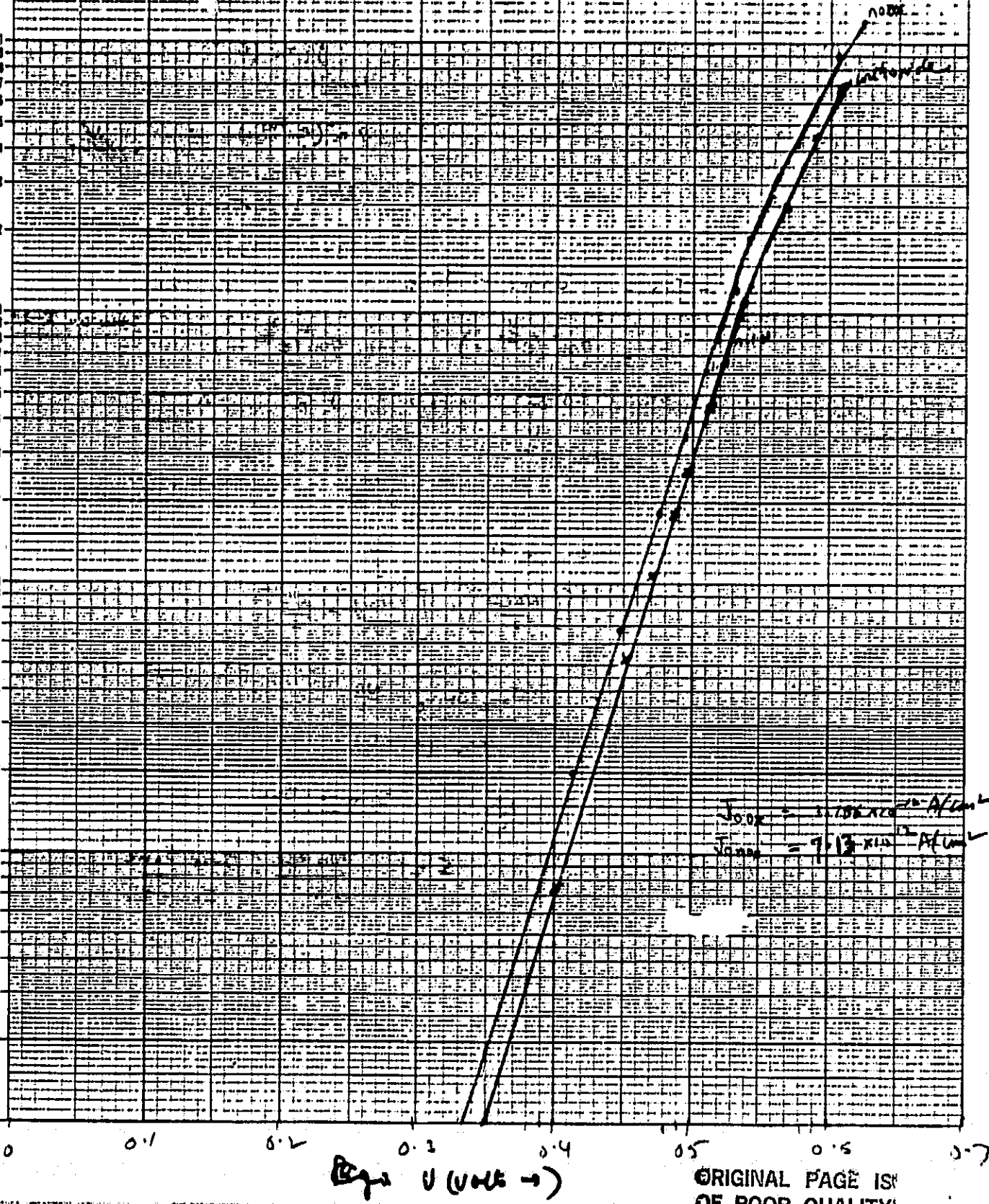


Fig 2.

(E-IR) vs (V-IR)

Figure 3

10<sup>-1</sup>  
10<sup>-2</sup>  
10<sup>-3</sup>  
10<sup>-4</sup>  
10<sup>-5</sup>





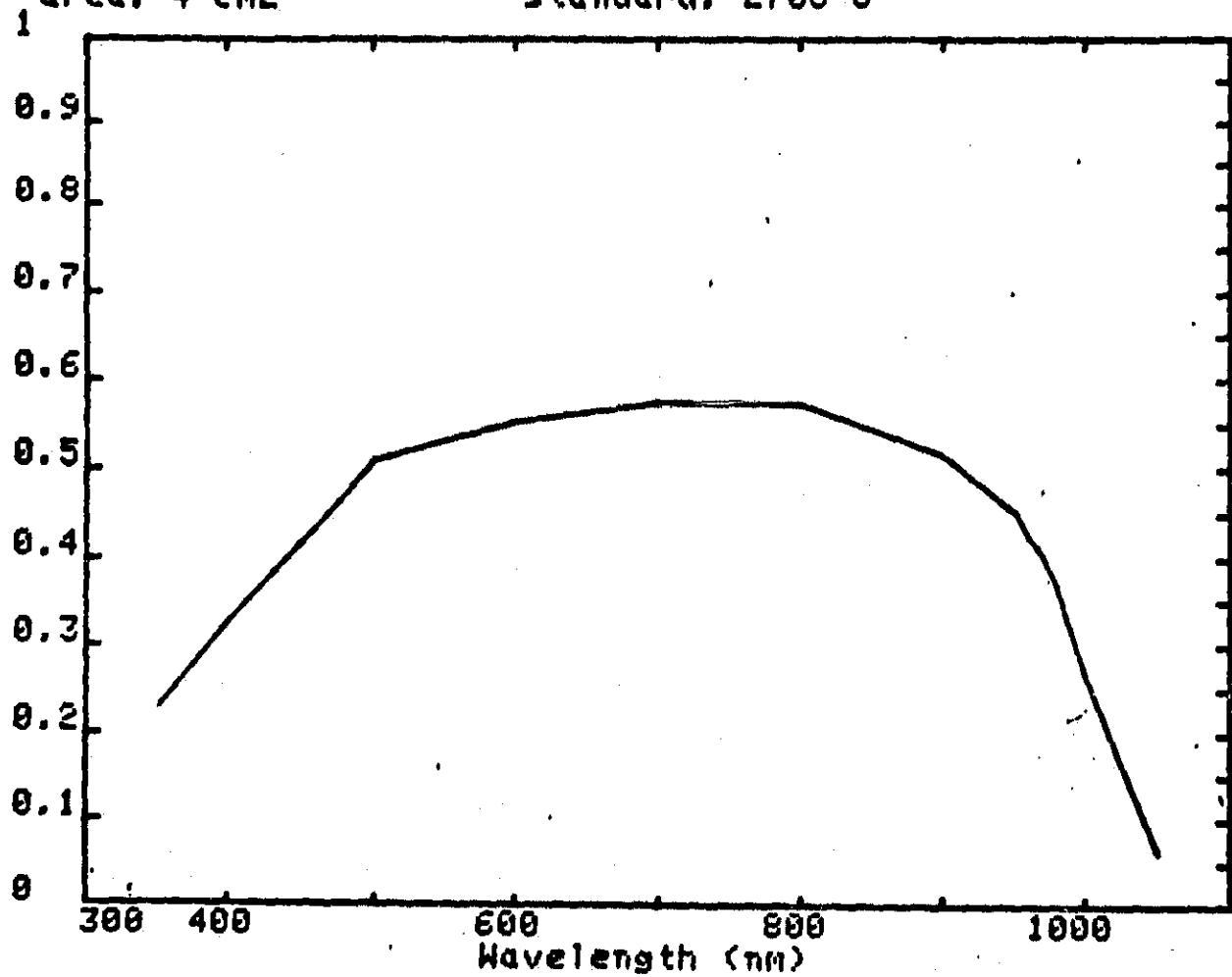
# EXTERNAL QUANTUM EFFICIENCY

Cell: 4412-5C

21-FEB-85 15:03:09

area: 4 cm<sup>2</sup>

standard: 2706-8



Pressure (psi)

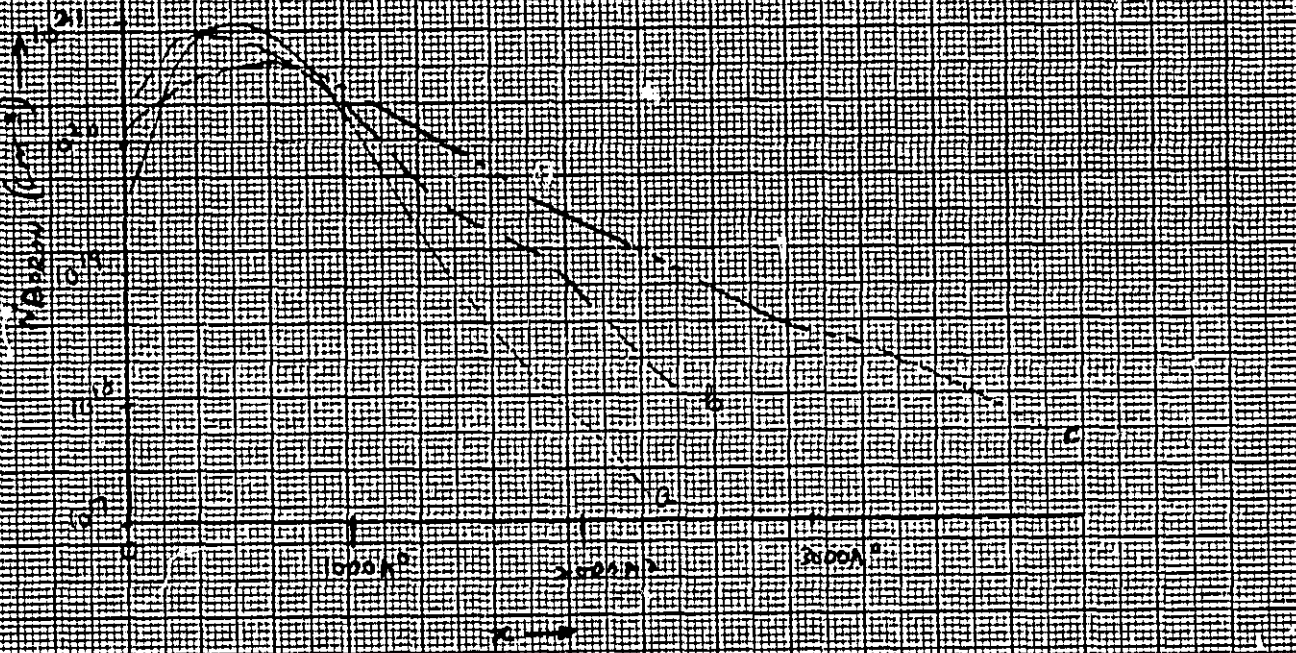
0.21  
0.15  
0.10  
0.05  
0.00

1000 psi

2000 psi

3000 psi

0.00



# Program Plan

| Program<br>Tasks/Subtasks  | Milestones |   |   |   |   |   |   |   |   |    |    |    |
|--|------------|---|---|---|---|---|---|---|---|----|----|----|
|  | 1          | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| 1. Effect of Low Energy H <sup>+</sup> Implants on Surface Properties            |            |   |   |   |   |   |   |   |   |    |    |    |
| A. Effect on Surface Recombination Velocity S                                    |            |   |   |   |   |   |   |   |   |    |    |    |
|  |            |   |   |   |   |   |   |   |   |    |    |    |
| B. Correlate S to the Surface Composition and Electrical Characteristics         |            |   |   |   |   |   |   |   |   |    |    |    |
|  |            |   |   |   |   |   |   |   |   |    |    |    |
| 2. Effect on Si Regrowth and Diffusion   |            |   |   |   |   |   |   |   |   |    |    |    |
| A. Effect on Diffusion of Boron, Arsenic, and Phosphorous                        |            |   |   |   |   |   |   |   |   |    |    |    |
|  |            |   |   |   |   |   |   |   |   |    |    |    |
| B. Effect on Regrowth After Si <sup>+</sup> Implants into Silicon                |            |   |   |   |   |   |   |   |   |    |    |    |
|  |            |   |   |   |   |   |   |   |   |    |    |    |
| 3. Emitter, Space Charge Region, and Base Passivation by H <sup>+</sup> Implants |            |   |   |   |   |   |   |   |   |    |    |    |
|  |            |   |   |   |   |   |   |   |   |    |    |    |
| 4. Hydrogen Passivation of Bulk Silicon Impurity Levels                          |            |   |   |   |   |   |   |   |   |    |    |    |
| A. Hydrogen Passivating or Gettering   |            |   |   |   |   |   |   |   |   |    |    |    |
|  |            |   |   |   |   |   |   |   |   |    |    |    |
| B. Hydrogen Passivation Influence by Background Carbon and Oxygen                |            |   |   |   |   |   |   |   |   |    |    |    |
|  |            |   |   |   |   |   |   |   |   |    |    |    |

(completed except for some additional modelling)

(more work needed to determine when oxygen enters layers; otherwise completed)

(completed)

(completed regrowth studies of As implanted layer; have not yet done Si implanted material)

(experimentation and modelling)

(experimentation)

(experimentation)

[illegible]